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THE EFFECT OF ORGANIC ADDITIVES ON THE STRUCTURAL CHARACTERISTICS OF LEAD DEPOSITS ELECTROWON FROM AQUEOUS CHLORIDE ELECTROLYTE

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THE EFFECT OF ORGANIC ADDITIVES ON THE STRUCTURAL CHARACTERISTICS OF LEAD DEPOSITS ELECTROWON FROM AQUEOUS CHLORIDE ELECTROLYTE

by

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ABSTRACT

The effect of certain organic additives on the structural characteristics of lead deposits electrowon from aqueous chloride electrolyte was determined using scanning electron microscopy and polarization techniques. All additives studied were ineffective at concentrations $\leq$100 mg/L in eliminating dendritic Pb formation. Glue additions in the range 300 to 600 mg/L minimized but did not prevent completely Pb dendrite formation. The combined addition of ECA and transtan eliminated Pb dendrites but the Pb deposits contained voids.

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EFFETS DES ADDITIFS ORGANIQUES SUR LES CARACTÉRISTIQUES STRUCTURALES DES DÉPÔTS DE PLOMB RÉCUPÉRÉS PAR EXTRACTION ÉLECTROLYTIQUE D'UNE SOLUTION AQUEUSE DE CHLORURE ÉLECTROLYTIQUE

par

D.J. Mackinnon* et J.M. Brannen**

RÉSUMÉ

On a déterminé à l'aide d'un microscope à balayage électronique et de techniques de polarisation l'effet de certains additifs organiques sur les caractéristiques structurales des dépôts de plomb récupérés par extraction électrolytique d'une solution aqueuse de chlorure électrolytique. Tous les agents d'addition étudiés se sont avérés impuissants à éliminer la formation de Pb (plomb) dentritique dans les concentrations de $\leq$100 mg/L. Des additions de colle dans la gamme de 300 à 600 mg/L ont minimisé mais n'ont pas empêché la formation de Pb dentritique. L'addition conjuguée des additifs organiques ECA et Transtan a éliminé les dentrites Pb mais les dépôts de Pb étaient poreux.

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INTRODUCTION

Existing and proposed regulations to control the lead smelter environment have led to an extensive study of lead extraction techniques to replace the present industrial sinter/blast furnace method for lead production. Hydrometallurgists have focused attention on chloride-based leach electrolysis processes (1-3). A major technical hurdle to overcome in these processes is the electrolysis step; failure to develop an environmentally and economically viable cell will severely curtail the commercialization of a chloride-based hydrometallurgical lead plant. At the present state of development, neither the fused salt nor the aqueous electrolysis concepts have advanced as a clear cut candidate for the recovery of lead metal, and fundamental studies should continue on both systems.

An advantage of the aqueous electrolysis system is that the ferric chloride leach solution is regenerated directly in the anode compartment of the cell, thus eliminating the need for handling Cl_2; also the oxidation of ferrous to ferric ion rather than chloride ion to Cl_2 results in a reduction in the voltage of the anodic reaction of about 0.6 volts, and hence an accompanying reduction in the energy requirement for lead electrowinning. Another energy-related advantage is the potential to operate the process isothermally; an environmental advantage results because the crystallization, washing and drying of $PbCl_2$ are eliminated.

Major technical problems to overcome for the aqueous system include: i) a very effective cementation step possibly combined with an ion exchange step is required for electrolyte purification if post electrolysis refining of lead is to be avoided; ii) if a compact, dense lead deposit cannot be obtained, then the lead should crystallize on the cathode in a fashion such that it will fall by its own weight, negating the need for a mechanical wiping device. Also, the lead, as it collects in the bottom of the cell must lend itself to easy removal and briquetting.

Lead electrodeposits from aqueous chloride electrolytes are characteristically non-compact and powdery, even at low current densities. Thus, attempts to produce smooth, dense, compact deposits of lead from such systems have met with only limited success. Cathodic polarization studies by Khan (4) showed that lead deposition from aqueous chloride electrolyte occurred with negligible overvoltage, a condition which hindered the formation of dense, compact deposits. The use of surface active and colloidal additives and increased electrolyte agitation did not significantly improve the quality of the deposit. Based on these results Khan concluded that the cathodic production of a non-adherent lead powder would be the most feasible means for recovering lead from chloride solution.

Pomosov et al. (5) used anion-active additives (Talon B, sulfite-cellulose caustic), molecular-type additives (tannin, urea, resorcinal, phenol) and ampholytes (glue, gelatin) in an unsuccessful attempt to electrowin compact lead deposits from aqueous chloride electrolytes. The ineffectiveness of these addition agents was attributed to strong specific adsorption of Cl^- on the cathode surface and to the inhibition of the diffusion of the additives to the cathode by the viscosity of the electrolyte.

However, Pomosov et al. (5) found that by adding "high" concentrations of both glue and phenol to the electrolyte, a compact lead deposit could be electrowon at 150 A/m^2 from a solution containing 13-26 g/L $PbCl_2$ and 195 g/L $CaCl_2$; the glue and phenol concentrations were 1.5 and 1.2 g/L respectively.

Kramer et al. (6) found that the addition of EZ3, a technical protein colloid (synthetic glue) promoted more compact deposits with fewer dendrites. The least dendritic deposit was formed when the solution contained 0.4 g/L glue and the electrolysis was done at low current density, 100 A/m^2. The presence of glue resulted in shinier deposits which adhered to the cathode surface.

Although some success has been achieved in obtaining compact lead deposits, these deposits were not completely dendrite-free nor were they the result of long-term (24 h) electrolysis. The present study was undertaken to determine the effectiveness of several additives in producing long-term, smooth, compact lead deposits from aqueous chloride electrolyte.

EXPERIMENTAL

The electrowinning cell and associated electrolyte circulation system is shown schematically in Figure 1. The cell consisted of three compartments: two anode compartments separated from a central cathode compartment by Dynel cloth diaphragms. The anode compartments were sealed to the atmosphere and the chlorine gas and spent electrolyte were withdrawn via glass tubes inserted through the anode compartment cover. The cathode compartment was fitted with a hinged cover with a slot allowing for easy removal of the cathode plus lead deposit for stripping. Vigorous agitation of the electrolyte at the cathode surface was achieved by pumping recirculated catholyte at high pressure through (sparging) holes at the bottom of the cathode compartment near the surface of the cathode. The feed electrolyte was introduced into the cathode compartment by the siphoning action of the recirculating loop. The feed rate was adjusted by means of a teflon-glass fine metering valve as required to maintain the concentration of Pb in the catholyte at 15 g/L. The feed delivery system was immersed in the temperature bath. The temperature of the feed (bottle) was 20°C higher than the cell temperature (75°C). A catnode area of (3.75 in^2) 24.20 cm^2 was used to contact the electrolyte. D.S.A. anodes, 0.1 cm thick extended through slots in the anode cover and electrical contacts were bolted to the exposed tops of the anodes. Current to the cell was provided by a d.c. rectifier (6-30 amp;

0-25 volt). The cumulative ampere-hours (total coulombs) were recorded using an ampere-time meter.

The electrolyte was prepared using reagent grade chloride materials. Unless otherwise stated the cell electrolyte contained 15 g/L Pb (as $PbCl_2$), 0.3 M HCl and 4.0 M NaCl. The feed solution composition was equivalent to the cell electrolyte except that it contained 30 g/L Pb. Organic addition agents were added at the desired concentration to both the feed and cell electrolytes from their respective stock solutions. The addition agents evaluated included: Pearl glue, Jaguar C-13, gelatin, Gum Arabic, Percol 140, Separan NP10, thiourea, tetrabutlyammonium chloride, glycine, tannic acid, transtan (liqnin sulphonate) and ECA (an aloes extract).

Cathodes were prepared from 1/16 inch sheets of 316 stainless steel, titanium, copper and nickel. Prior to use in the cell, the exposed surface of the cathode was hand polished using 600 grit polishing paper. Current densities of 161 and 323 A/m^2 were used for the experiments. Unless stated otherwise, the electrolyses were run for 6 h. At the end of the electrolysis period, the cathode was removed from the cell and rinsed with water prior to stripping the lead deposit.

The effect of selected addition agents on the polarization curves for Pb deposition from aqueous chloride electrolyte were determined using an EG&G Model K47 Corrosion Cell system. Potentiodynamic polarization curves were measured using an EG&G Model 173 potentiostat driven by an EG&G Model 175 numerical programmer. The current-potential curves were recorded using a Hewlett Packard Model 7004B X-Y recorder. The graphite working electrode (area 3.80 cm^2) was centered between two graphite anodes (counter electrode). All potential values were measured vs a saturated calomel reference electrode (SCE). The electrolyte used for the polarization

measurements consisted of 4.0 M NaCl + 0.3 M HCl + 10 g/L $PbCl_2$ maintained at 70°C. The polarization curves were determined over the potential region -0.4 to -0.7 V vs SCE at a scan rate of 5 mV/s.

RESULTS AND DISCUSSION

PRELIMINARY TESTS

Preliminary tests were carried out in order to screen the various organic additives for their effectiveness in eliminating dendritic lead growth. Low concentrations of these additives; i.e., $\leq$100 mg/L, were completely ineffective in terms of eliminating lead dendrites. Additives such as glue, tannic acid, ECA and transtan at concentrations >100 mg/L, showed some promise in eliminating dendritic growth and these were studied in more detail.

POLARIZATION STUDIES

The effect of various concentrations of glue, glycine and tannic acid on lead deposition polarization is shown in a series of polarization curves, Figures 2-4. As indicated in Figure 2, the addition of up to 2.0 g/L glycine had no effect on the lead deposition polarization curve. The addition of 0.6 g/L glue resulted in a small increase in lead deposition polarization, Figure 3, but higher glue concentrations actually depolarized the reaction. The addition of 0.6 g/L tannic acid, Figure 4 produced a significant increase in lead deposition polarization which increased with further additions of tannic acid, up to 2.0 g/L.

Both the individual and combined effects of ECA and transtan on lead deposition polarization were studied. The effect of ECA at 1.0 and 2.0 g/L is shown in Figure 5. Compared to the addition-free curve, 1.0 g/L ECA

caused a significant increase in lead deposition polarization; increasing ECA to 2.0 g/L resulted in no significant change in polarization compared to 1.0 g/L ECA. The addition of transtan, Figure 6, also resulted in a significant increase in lead deposition polarization with the effect of 4.0 g/L transtan being slightly greater than that for 2.0 g/L transtan. The polarization curve obtained in the presence of transtan was characterized by an initial current plateau region followed by a sharp rise in current as the potential increased.

The combined additions of ECA and transtan, Figure 7, resulted in a further increase in lead deposition polarization compared to the individual additives, with the shape of the curve being similar to that of transtan alone, except that the current rise, which occurred after the plateau region, was more gradual for the combined additives.

DEPOSIT CHARACTERISTICS

In the absence of addition agents, the lead deposits were non-compact, poorly adherent and dendritic, particularly at the edges of the cathode. A portion of the non-dendritic part of such a deposit is shown in the SEM photomicrograph, Figure 8. It consists of isolated clusters of metal with numerous voids.

The addition of glycine in the range 0.5 to 2.0 g/L had no beneficial effect on the lead deposits. In fact, the higher glycine concentrations promoted dendritic growth. As indicated in the previous section, the addition of 2.0 g/L glycine had no effect on lead deposition polarization.

The addition of glue (0.3 to 0.6 g/L) resulted in an improved lead deposit with fewer and smaller dendrites. This is in agreement with the polarization studies which showed that glue concentrations in this range resulted in an increase in lead deposition polarization. As indicated in

the previous section, higher glue concentrations (>0.6 g/L) depolarized lead deposition and were subsequently found to result in more granular lead deposits and increased dendritic growth.

Although increasing concentrations of tannic acid (0.5 to 2.0 g/L) produced a significant increase in lead deposition polarization, they had no significant effect on the lead deposits which remained predominantly dendritic.

A combination of two additives, aloes and lignin sulphonate, are used effectively by Cominco to control the surface and edge quality of the lead cathode deposits in the electrorefining of lead (7). Aloes is a natural plant extract and lignin sulphonate is a byproduct of pulp and paper manufacture. Various combinations of these two additives; viz., aloes (ECA) and lignin sulphonate (transtan), were very effective in increasing lead deposition polarization and their effect on the lead deposit characteristics in chloride electrolyte was also determined. The combined presence of ECA and transtan in the electrolyte effectively eliminated dendritic growth over the 6-h deposition time. The most effective combination was 2 g/L ECA + 1 g/L transtan which produced granular, metallic deposits with no dendrites. The morphology of such a deposit is shown in the SEM photomicrograph, Figure 9(a) and consists of clusters of irregularly shaped crystals with voids between the clusters.

The deposit obtained from an electrolyte containing 4 g/L transtan + 1 g/L ECA consisted of metallic platelets and loose powder. The deposit morphology, Figure 9(b), is composed of flat platelets with prominent grain boundaries. Such a deposit crumbles into small pieces when it is stripped from the cathode.

CONCLUSIONS

Organic additives at concentrations $\leq$100 mg/L in aqueous lead chloride electrolyte did not inhibit dendritic lead growth. Glue concentrations in the range 300-600 mg/L resulted in a small increase in lead deposition polarization and reduced the size of the lead dendrites. Higher glue concentrations, however, depolarized lead deposition and increased dendritic growth.

Glycine additions up to 2.0 g/L had no effect on lead deposition polarization nor on the structure of the lead deposit. Although the addition of tannic acid increased lead deposition polarization it was not effective in minimizing dendritic growth.

The presence of ECA and transtan in the electrolyte effectively eliminated lead dendrite formation but the deposits were not compact.

The ineffectiveness of these addition agents in producing compact lead deposits even at low current density suggests that further work on this system should be directed toward developing a cell and electrolysis conditions capable of producing uniform lead crystals that readily fall from the cathode.

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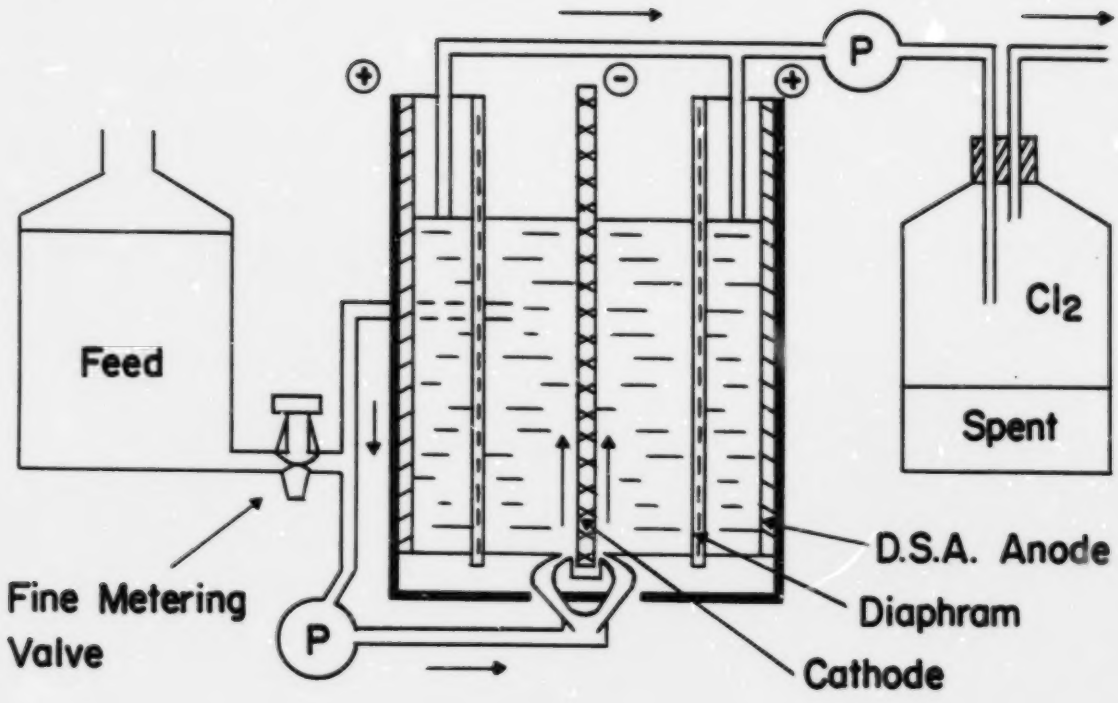


Fig. 1 - Schematic drawing of the electrowinning cell.

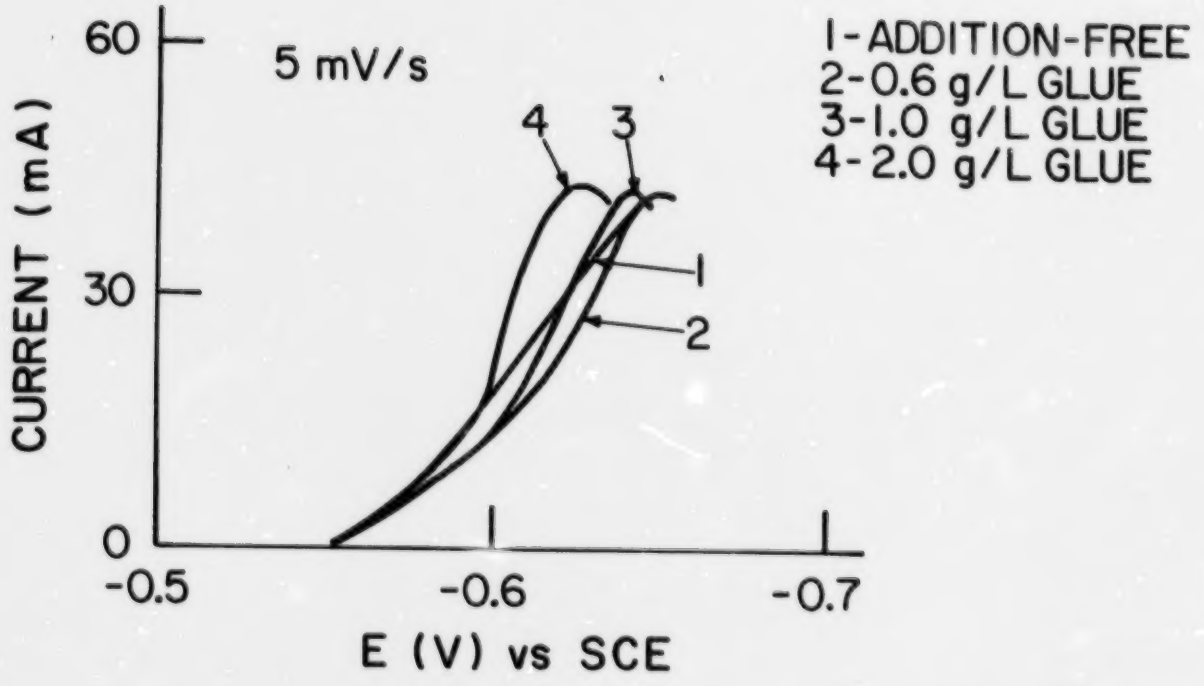


Fig. 2 - Current-potential curves showing the effect of glue on lead deposition polarization.

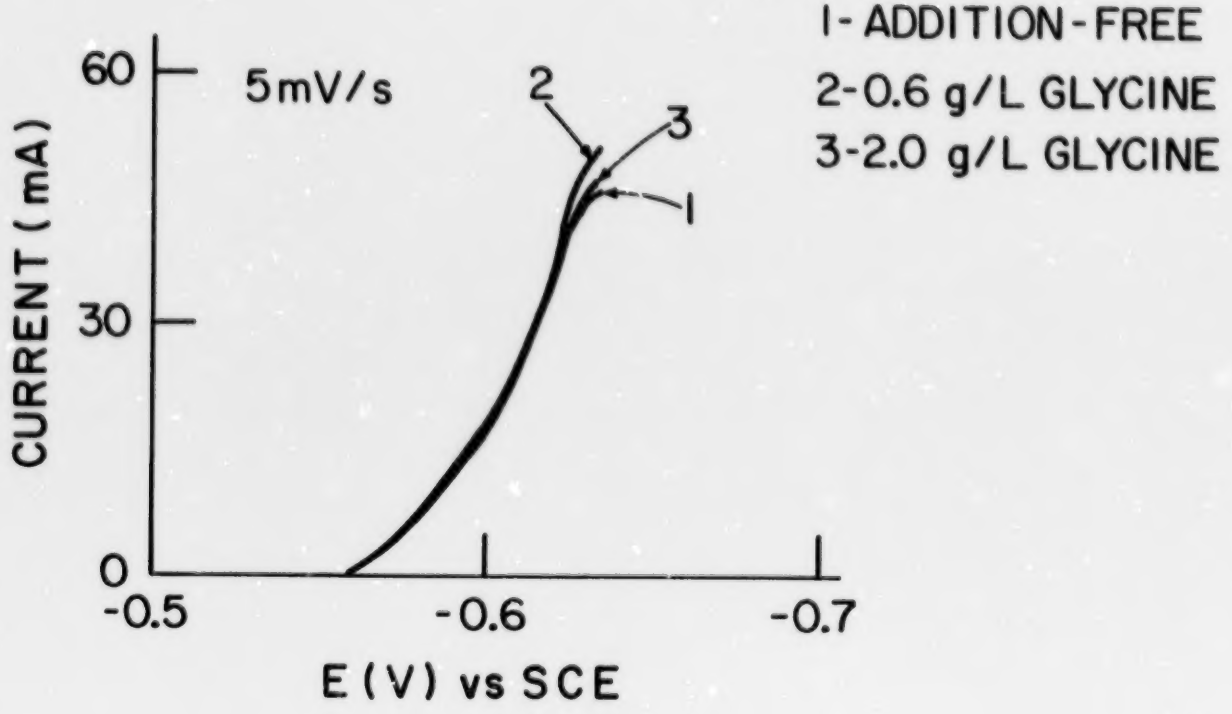


Fig. 3 - Current-potential curves showing the effect of glycine on lead deposition polarization.

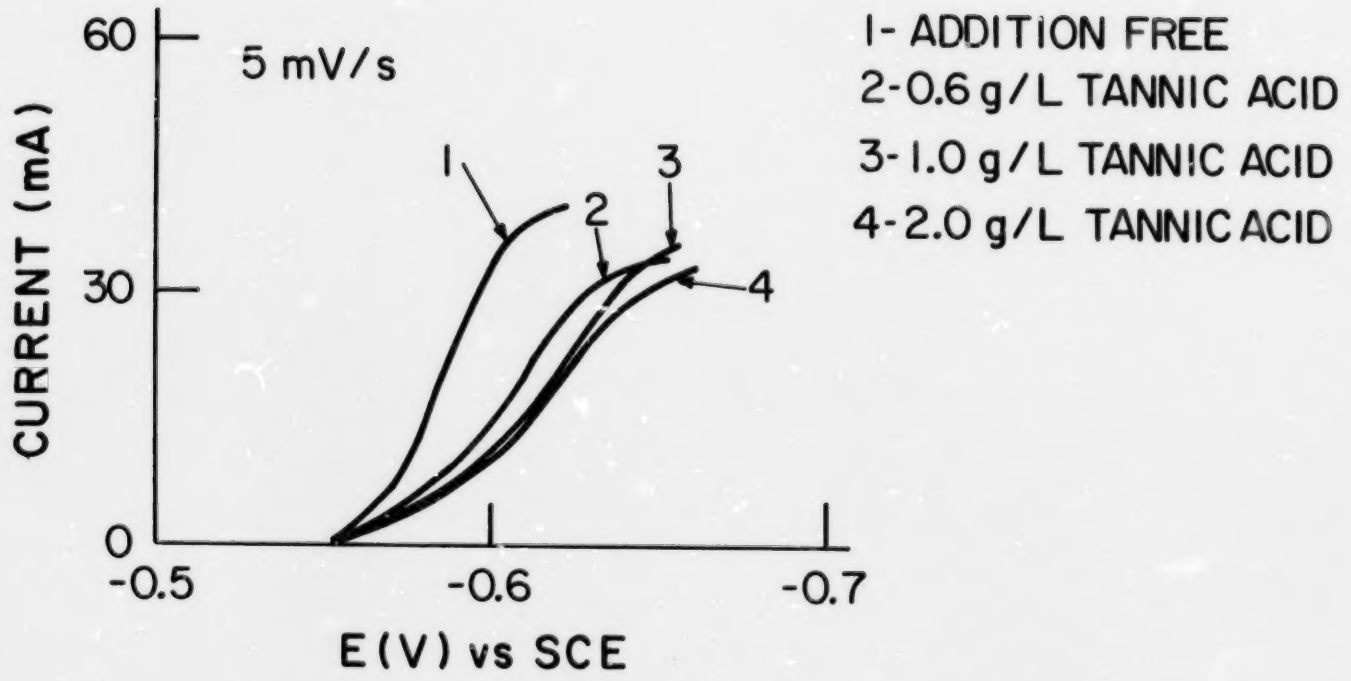


Fig. 4 - Current-potential curves showing the effect of tannic acid on lead deposition polarization.

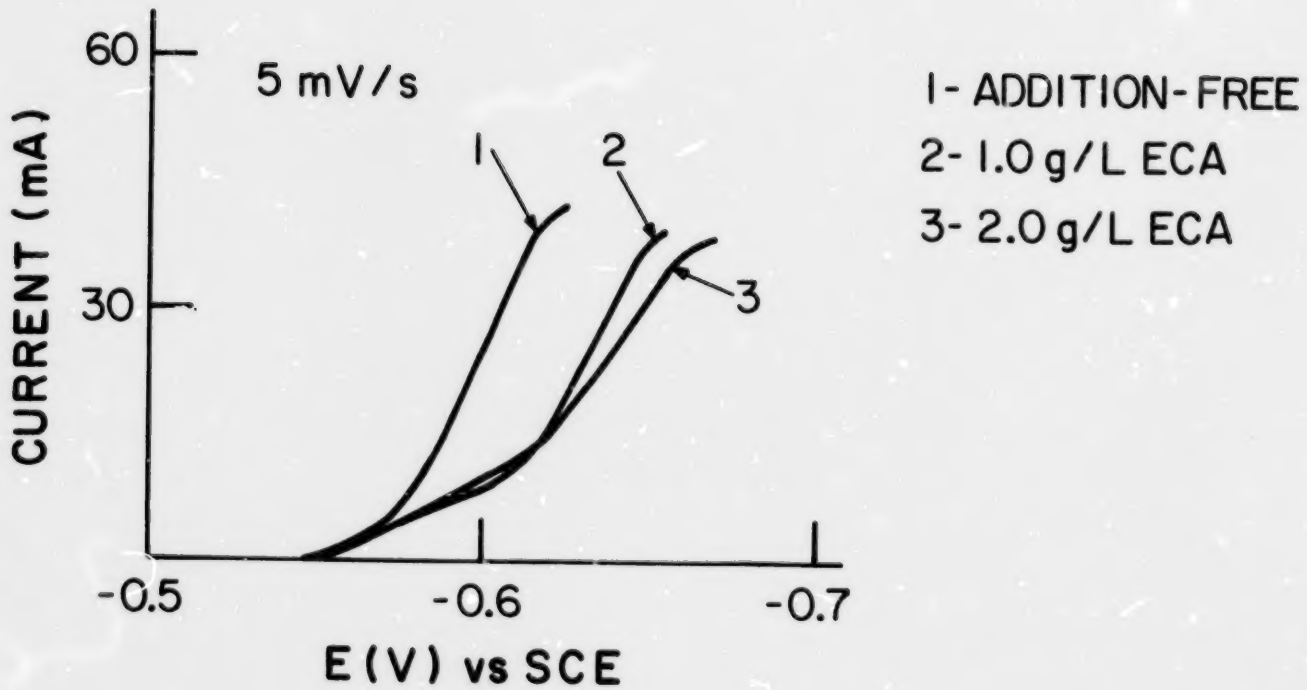


Fig. 5 - Current-potential curves showing the effect of ECA on lead deposition polarization.

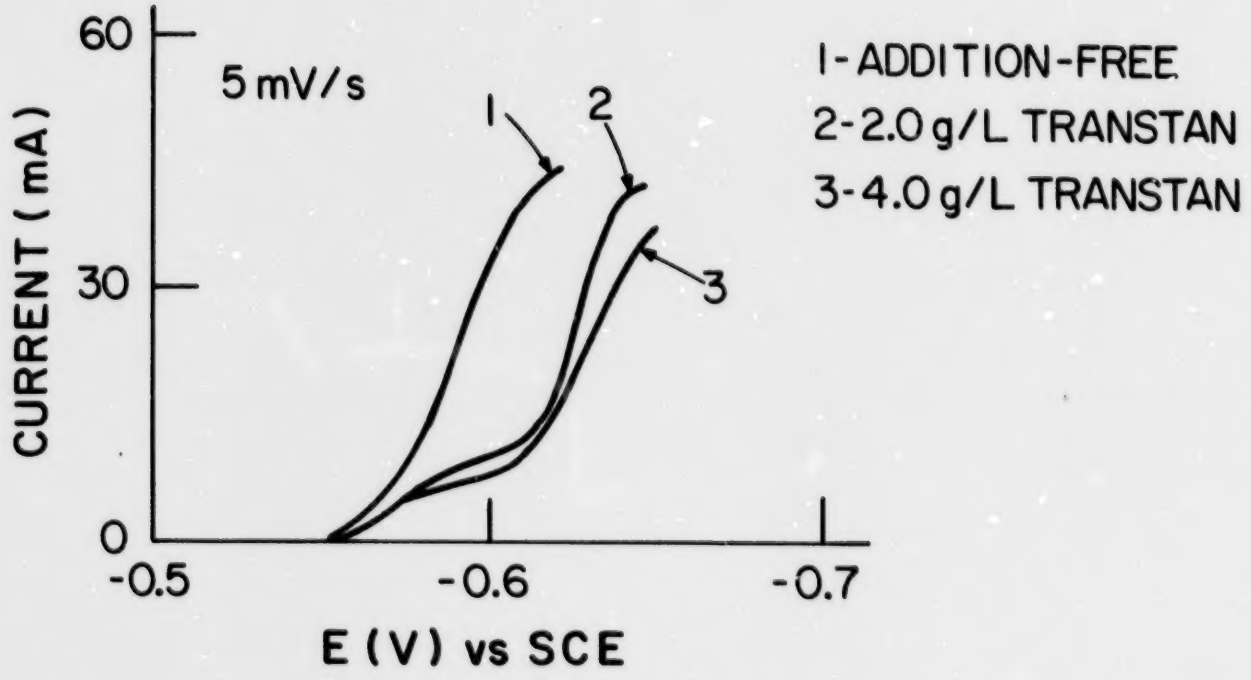


Fig. 6 - Current-potential curves showing the effect of transtan on lead deposition polarization.

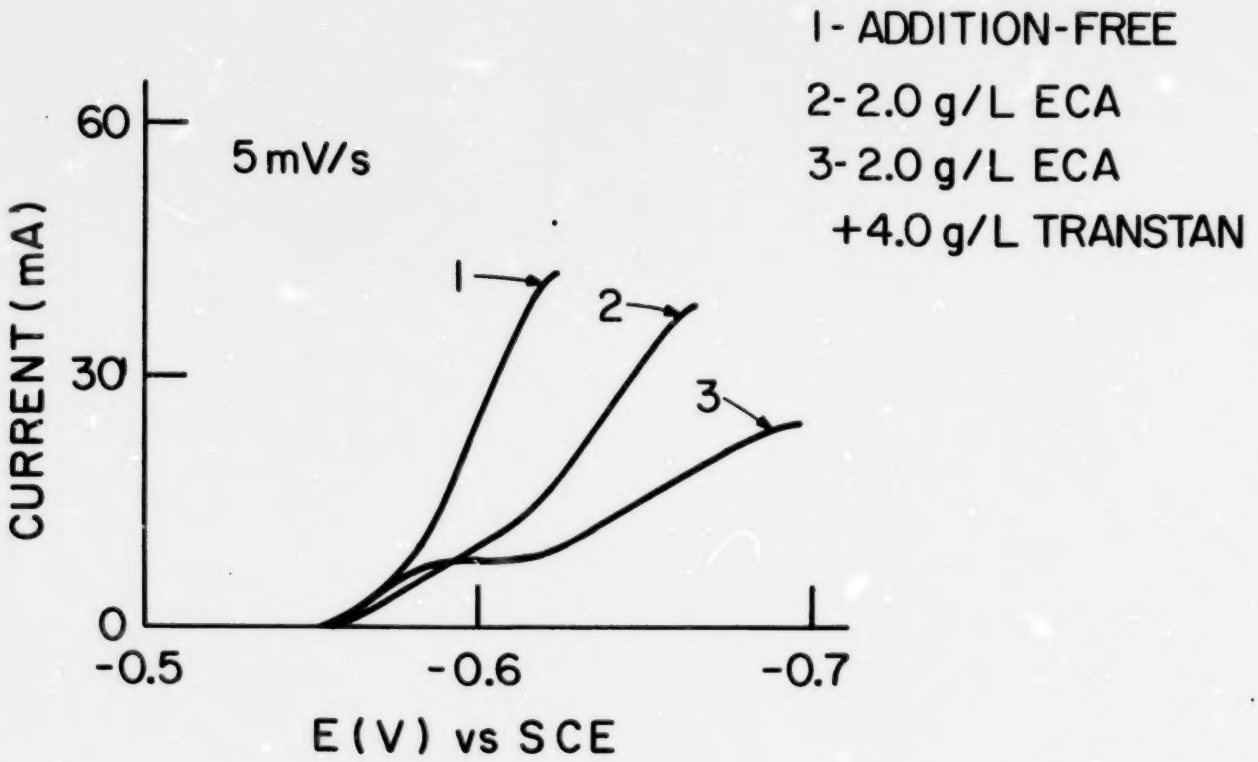
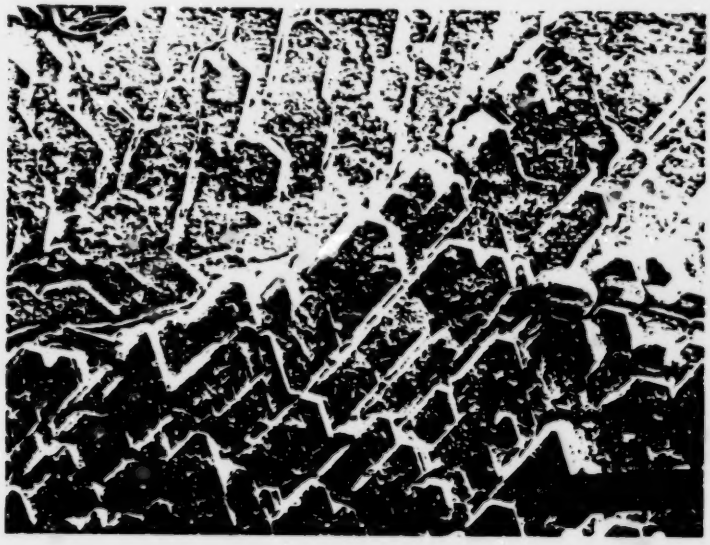


Fig. 7 - Current-potential curves showing the effect of ECA + transtan on lead deposition polarization.

Figure 8. SEM photomicrograph showing the lead deposit morphology obtained at 161 A/m^2 from a solution containing 15 g/L Pb, 3.0 M NaCl + 0.3 M HCl - addition-free.

a) 2 g/L ECA + 1 g/L Transtan



b) 1 g/L ECA + 4 g/L Transtan

Figure 9. SEM photomicrograph showing the effect of ECA and transtan on the morphology of lead deposits obtained at 161 A/m^2 from a solution containing 15 g/L Pb, 3.0 M NaCl + 0.3 M HCl.